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(21) International Application Number: PCT/GB95/02781 (22) International Filing Date: 28 November 1995 (28.11.95) (30) Priority Data: 9425105.5 13 December 1994 (13.12.94) GB (71) Applicant (for all designated States except US): BP CHEMICALS LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): ELLIS, Brian [GB/GB]; 44 Sunmead Road, Lower Sunbury, Middlesex TW16 7LN (GB). (74) Agent: KRISHNAN, Suryanarayana, Kalyana; BP International Limited, Group Patents & Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).		(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG). Published <i>With international search report.</i>
(54) Title: IONIC LIQUIDS (57) Abstract <p>This invention relates to a process for making ionic liquids by reacting a solution of a lead salt of an anion desired in the ionic liquid with a solution of a halide of a cation desired in said ionic liquid, separating the precipitate of the lead halide so formed to leave behind a solution of the desired ionic liquid. Ionic liquids are versatile and can be used as catalysts in a number of hydrocarbon conversion reaction such as e.g. alkylation, oligomerisation, isomerisation and polymerisation.</p>		

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IONIC LIQUIDS

This invention relates to a method of making ionic liquids using relatively inexpensive reactants.

Ionic liquids are primarily salts or mixtures of salts which melt below room temperature. Such salts or mixtures comprise a cation and an anion and the anion itself may be a salt such as eg haloaluminate. Thus, ionic liquids include in various combinations one or more anions such as eg haloaluminates, nitrates, sulphates, fluoroborates and acetates in combination with one or more cations such as imidazolium, pyridinium and phosphonium cations each of which may carry hydrocarbyl substituents. Examples of the source of cations include one or more of 1-methyl-3-butyl imidazolium halides, 1-butyl pyridinium halide and tetrabutyl phosphonium halides.

It is known to prepare such ionic liquids by various methods. For instance, in J Chem. Soc. Chem. Comm. 965 (1992), Wilkes et al describe a method of preparing ionic liquids which involves:

(i) mixing a methanol-water solution of a silver salt of an anion such as the acetate, tetrafluoroborate, nitrate or sulphate with a methanol-water solution of an equimolar amount of 1-ethyl, 3-methyl-imidazolium chloride, (ii) filtering off the resultant precipitate of silver chloride and (iii) evaporating the solvent to leave behind the ionic liquid so formed. Whilst the process is very efficient, it is relatively uneconomic in that silver salts are relatively expensive. It has now been found that such ionic liquids can be prepared by using relatively inexpensive raw materials.

Accordingly, the present invention is a method for making ionic liquids said process comprising reacting a solution of a lead salt of an anion desired in the ionic liquid with a solution of a halide of a cation desired in said ionic liquid, separating

the precipitate of the lead halide so formed to leave behind a solution of the desired ionic liquid.

The lead salt used to make the desired ionic liquid may be selected from the group comprising acetate, fluoroborate, nitrate and sulphate. The salt of the cation
5 reacted with the lead salt may be selected from the group comprising an imidazolium chloride, a pyridinium chloride, a phosphonium chloride, and hydrocarbyl substituted derivatives of such cations. Examples of such cations include H-pyridinium; alkyl pyridinium; alkyl, alkyl imidazolium; trialkyl, alkyl phosphonium; and trialkyl, alkyl ammonium. Each of the hydrocarbyl groups such
10 as alkyl groups in such cations may contain 2-20 carbon atoms.

The two salts, suitably in equimolar proportions, are suitably reacted together in the form of their respective solutions, suitably an aqueous alcoholic solutions eg in aqueous methanol. The aqueous alcoholic solution suitably contains alcohol and water in a volume ratio of about 4:1. The reaction can be
15 carried out at ambient temperature and the resultant precipitate of lead chloride can be separated from the solution by filtration. In order to enable completion of the reaction, it is preferable to allow the filtrate resulting from separation of the initial deposit of lead chloride precipitate to stand for a further period of time. This is suitably carried out by leaving the solution to stand overnight in a cool place such
20 as eg a refrigerator so that any lead chloride (which has a small solubility in water at ambient temperature) remaining in solution can separate out and is removed by a further filtration. Thereafter, the solvent component of the filtrate can be removed by conventional methods such as eg distillation or rotary evaporation to leave behind the desired ionic liquid.

25 The method described above can be used to make ionic liquids from any cations derivable from a cation selected from imidazolium, pyridinium or phosphonium halides or the hydrocarbyl substituted derivatives thereof, especially those cations which include H-pyridinium; alkyl pyridinium; alkyl, alkyl imidazolium; trialkyl, alkyl phosphonium; and trialkyl, alkyl ammonium.

30 Ionic liquids made by the method of the present invention can be used in all known reactions where such ionic liquids function as catalysts such as eg oligomerization, polymerization and alkylation reactions.

The present invention is further illustrated with reference to the following Examples.

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EXAMPLE 1:**Preparation of 1-Butyl, 3-methylimidazolium nitrate:**

Lead nitrate (0.2 M) was dissolved in a solution (400 ml) of methanol in water (4:1 v/v). Not all the solid dissolved so a further 100 ml of distilled water was added
5 and the solution refluxed until all the white solid had dissolved. Butyl, methyl imidazolium chloride (0.2 M) was also dissolved in a solution (100 ml) of methanol in water (4:1 v/v) and then added to the lead nitrate solution. A white precipitate was formed. The mixture was then refluxed at 70-100°C approximately for 30 minutes and then left to cool to ambient temperature. The cooled solution was
10 filtered to separate the precipitate and the filtrate was then left in a refrigerator to allow further precipitation of any dissolved lead chloride. This was then filtered again and the filtrate recovered. The aqueous methanol solvent was removed from the second filtrate by evaporation under vacuum at about 100°C for approximately 90 minutes. A yellow ionic liquid comprising 1-butyl, 3-methyl imidazolium nitrate
15 substantially free of solvent was recovered.

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Claims:

1. A process for making ionic liquids said process comprising reacting a solution of a lead salt of an anion desired in the ionic liquid with a solution of a halide of a cation desired in said ionic liquid, separating the precipitate of the lead halide so formed to leave behind a solution of the desired ionic liquid.
- 5 2. A process according to Claim 1 wherein the lead salt used to make the desired ionic liquid is selected from the acetate, fluoroborate, nitrate and sulphate.
3. A process according to Claim 1 or 2 wherein the salt of the cation reacted with the lead salt is selected from an imidazolium chloride, a pyridinium chloride, a phosphonium chloride and the hydrocarbyl substituted derivatives of such cations.
- 10 4. A process according to any one of the preceding Claims wherein the cation reacted with the lead salt is selected from the group: H-pyridinium; alkyl pyridinium; alkyl, alkyl imidazolium; trialkyl, alkyl phosphonium; and trialkyl, alkyl ammonium.
5. A process according to Claim 3 or 4 wherein each of the hydrocarbyl groups in the cations contain from 2-20 carbon atoms.
- 15 6. A process according to any one of the preceding Claims wherein the lead salt and the salt of the cation are reacted together in equimolar proportions in the form of their respective solutions.
7. A process according to Claim 6 wherein the salts are in the form of their aqueous alcoholic solutions.
- 20 8. A process according to Claim 6 wherein the aqueous alcoholic solutions contain the alcohol and water in a volume ratio of about 4:1.
9. A process according to any one of the preceding Claims 6-8 wherein the reaction is carried out at ambient temperature and the resultant precipitate of lead chloride can be separated from the solution by filtration.
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10. A process for producing ionic liquid according to any one of the preceding Claims and as hereinbefore described with reference to the Examples.

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INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/GB 95/02781

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JOURNAL OF THE CHEMICAL SOCIETY, CHEMICAL COMMUNICATIONS, 1992 LETCHWORTH GB, pages 965-967, WILKES J S ET AL. 'Air and Water Stable 1-Ethyl-3-methylimidazolium Based Ionic Liquids' see the whole document	1-10
A	FR,A,1 318 190 (ARMOUR AND CO.) 10 May 1963 see claims 1-6	1,2,4,5, 7,9,10
A	EP,A,0 443 167 (BAYER AG) 28 August 1991 see column 3, line 12 - column 5, line 23	1,3-10

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☒ Further documents are listed in the continuation of box C.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 558 187 (BP CHEMICALS LTD.) 1 September 1993 see page 2, line 1 - line 15 see page 3, line 12 - line 21; claims 1-10 ---	1,3-5
A	FR,A,2 626 572 (INSTITUT FRANCAIS DU PETROLE) 4 August 1989 see page 1, line 32 - page 3, line 32 ---	1,3-5
A	EP,A,0 448 445 (INSTITUT FRANCAIS DU PETROLE) 25 September 1991 see claims 1-20 ---	1,3-5
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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